Our nuclear stockpile is getting older. Livermore scientists are collecting the

A Better Picture of Aging Materials

data and developing the models needed to predict how much aging is acceptable.

NUCLEAR weapons are complex systems made of many different materials and interconnecting components. The materials may interact with air, moisture, and environmental hazards during manufacture, shipping, storage, and assembly as well as with each other once they have been enclosed in the weapon. They may weaken, harden, corrode, or even fail. These changes in properties, whether chemical, physical, or mechanical, are often lumped together under the label "aging."

The shelf life of a nuclear weapon was not a major issue until the early 1990s when the U.S. ceased to develop and test nuclear weapons. Before that, new weapons featuring the latest technology were regularly designed and built. When a new weapon entered the stockpile, an older one was generally retired. Now, there are no new weapons, and existing weapons are expected to remain operational for many decades—to perform exactly as designed if they must ever be used.

The Department of Energy's Stockpile Stewardship Program has many facets, one of which is to analyze the aging processes of the materials used in nuclear weapons, such as high explosives, uranium, plutonium, organic materials, and polymers. This analysis builds on work that materials scientists at Lawrence Livermore have been doing since the inception of the Laboratory. In the past, they studied how various materials aged and interacted under stockpile conditions to provide guidance on the selection and use of the best available materials for Livermore's new weapons. Today, the mandate for materials scientists is more complex: to predict the lifetime of key weapon materials and to develop "age-aware" material models for use in codes that predict the lifetime of the overall weapon system.

Livermore chemist James LeMay is one of the coordinators assigned to this challenging set of activities. He and his colleagues are focusing primarily on the aging of the many organic materials used in a weapon. They are also examining the aging of high explosives and the interactions (compatibility) of the many materials in a nuclear weapon.

Data for Predictions

LeMay notes, "True scientific prediction, as opposed to a statistical projection, of how weapon materials age and interact with one another over time is difficult. Accurate predictions require excellent data, sophisticated models, and powerful, modern computers."

The data come from several sources. One is controlled laboratory experiments on weapon materials. They determine the properties of the materials before they begin to age, what environmental forces act upon them while they are enclosed in the weapon, and how those forces change the properties that are relevant to the performance of the system. In other words, a major focus of the work is on the fundamental science of materials.

Another source of data is the detailed characterization of components taken from the stockpile to determine how their relevant properties have changed (Figure 1). These measurements supplement DOE's Core Surveillance Program to verify the safety and reliability of U.S. nuclear weapons. Under core surveillance, weapons are removed from the stockpile on a regular basis and disassembled. Components are tested to assure that they operate as they did when the weapon was assembled. Under the newer Enhanced Surveillance Program, more detailed and fundamental experiments seek out previously unknown aging mechanisms that may affect a material's lifetime and allow scientists to extrapolate future aging trends from changes that have already occurred.

With accurate predictive models, researchers should be able to reduce the required number of system-level evaluations, which are expensive. Robust models would reflect what chemical or physical alterations in a material are under way and at what point component or weapon performance is affected. Surveillance could then be directed to look for predicted changes and to find previously unanticipated ones, thus providing a means for continual improvement and validation of predictive models. "We've got a long way to go," says LeMay, "but we have made considerable progress."

How Much Change Is OK?

Some materials in a nuclear weapon are designed to be marginally unstable.

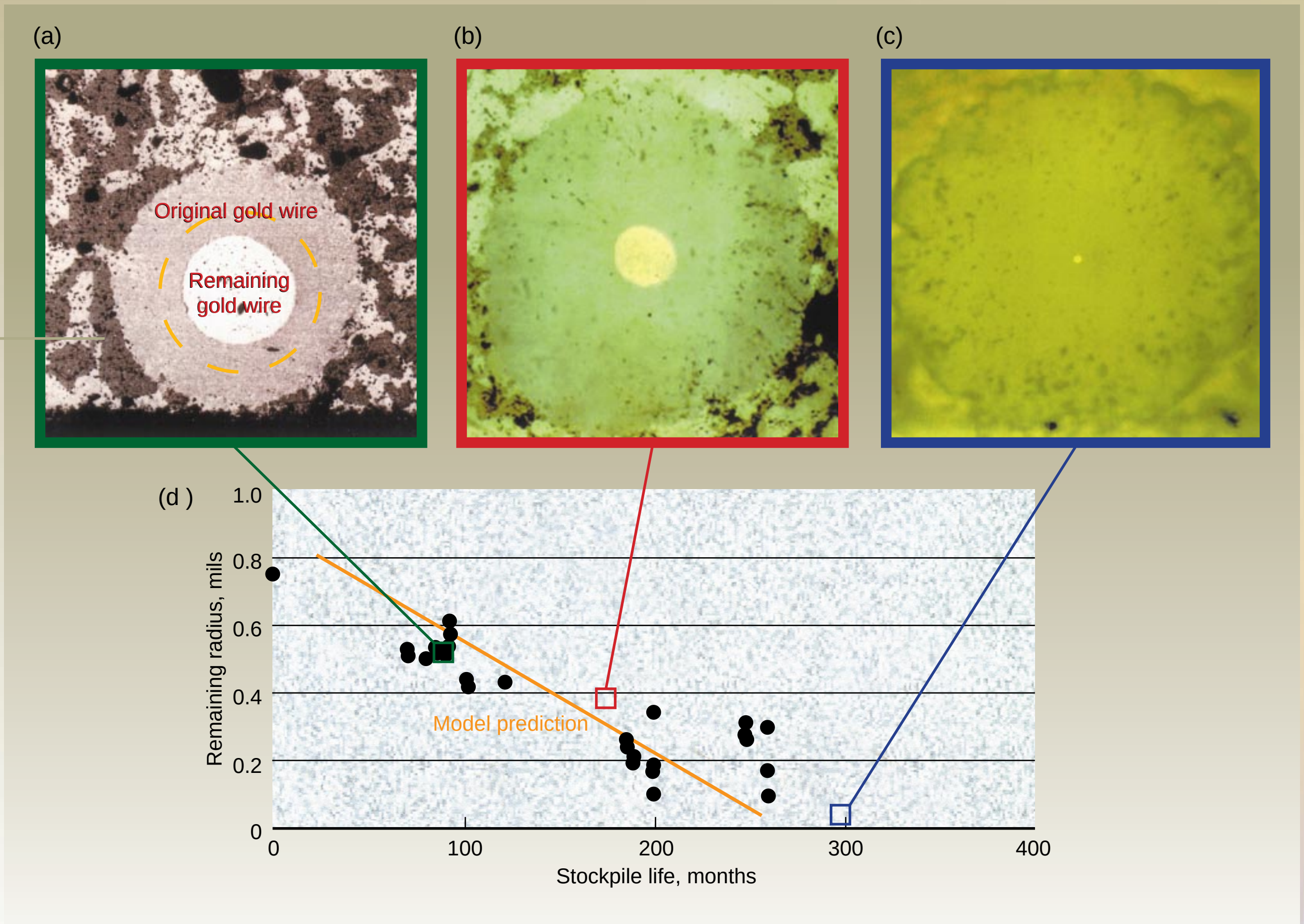


Figure 1. A multidisciplinary weapons program team at Livermore has studied the aging of the gold detonator bridgewires in previously stockpiled weapons. (a), (b), and (c) Cross sections of detonators removed from a previously stockpiled weapon. They illustrate the conversion of the bridgewire from gold to gold indide over the course of about 25 years. Gold indide has mechanical and electrical properties quite different from those of gold. (d) The predictive model in the graph indicates that these gold bridgewires corrode dramatically as they age. Actual aging data match the predictive model extremely well.

The high explosives used for initiation must be somewhat sensitive or they will not detonate. Radioactivity adds another dimension of instability. Even those parts that are theoretically stable can present difficulties. A bit of oil may be left on a part during manufacture. A trace of water vapor might appear in the system, causing corrosion. A seal might leak and admit oxygen and water. Materials that appeared to be pure at the time of manufacture may prove to be incompatible and react with one another. In all cases, these aging processes and interactions are extremely slow.

When a weapon is assembled, its array of components is not in thermodynamic equilibrium. Unfortunately, it is a basic law of nature that all of the parts in a closed system will strive for thermodynamic equilibrium. They will change and perhaps degrade by exchanging energy until equilibrium is achieved. In a nuclear weapon, that process would take a long time, but some components change faster than others and can cause unacceptable aging.

At some point in the degradation process—probably long before global thermodynamic equilibrium is achieved—the weapon will cease to be viable. One or more of its parts may have changed just enough or even failed such that the weapon no longer performs as required. An assumption of Livermore's materials aging studies is that there is a slightly earlier point where considerable aging has occurred and yet the weapon still operates as designed. LeMay likens it to an older automobile that still runs well but whose brakes are rather worn, whose tires are a bit flat, and whose engine does not turn over quite as quickly in the morning. The important questions are: Where is that point for a nuclear weapon? How much change is OK for the individual materials in the weapon?

The Materials at Hand

Livermore-designed nuclear weapons that reside in the stockpile have various configurations. But they generally incorporate plutonium, uranium, high explosives, plastics, adhesives, foams, and other materials that together make the weapon generate its designed yield.

To date, many changes related to aging and to incompatibilities between weapon materials have been observed. In the six high explosives used in various weapons, changes include swelling, plasticizer migration, binder degradation, mechanical property degradation, adhesive bond rupture, and incompatibilities. In addition, changes related to load retention and compression were found in the polymer foam cushions that provide padding between various weapon components.

Uranium, plutonium, lithium, and even gold exhibit surface corrosion. Several materials are affected by radiation from uranium and plutonium. Researchers also found incomplete curing, depolymerization, and hydrogen outgassing in some silicone compounds. In plastic parts, some polycarbonate material was degraded by ammonia gas emitted from a nearby component. An undesirably strong adhesion has developed between some plastic components. Some adhesives have incompletely cured, some are outgassing, and some bonds have weakened.

Organic materials are a particular concern. By their very nature, they can be less stable than many other materials. They have weaker bonds and tend to be reactive. They also are more readily damaged by the radiation that emanates from uranium and plutonium. Nevertheless, organics are an essential part of a weapon. Some serve chemical functions such as hydrogen “getters,” which absorb damaging hydrogen in a weapon’s hermetically sealed environment.

Other organics (such as silicone stress cushions, adhesives, and coatings) fill gaps, transmit loads, and mitigate vibration and shock, allowing a weapon to survive what is known as the stockpile-to-target sequence (STS). A weapon sitting in the stockpile encounters few traumas, but during the STS, it must endure transport on a truck, temperature changes during storage, and perhaps ultimately a launch and flight from under the wing of a plane, from a submarine, or from a land-based missile silo.

For experiments that examine everything from bulk materials to individual atoms, Livermore scientists are using a unique collection of tools to examine and test the surfaces and structure of the many materials that make up a weapon. Some of these tools were developed at Livermore. Others were developed elsewhere but modified at Livermore for use in the stewardship of the U.S. nuclear arsenal.

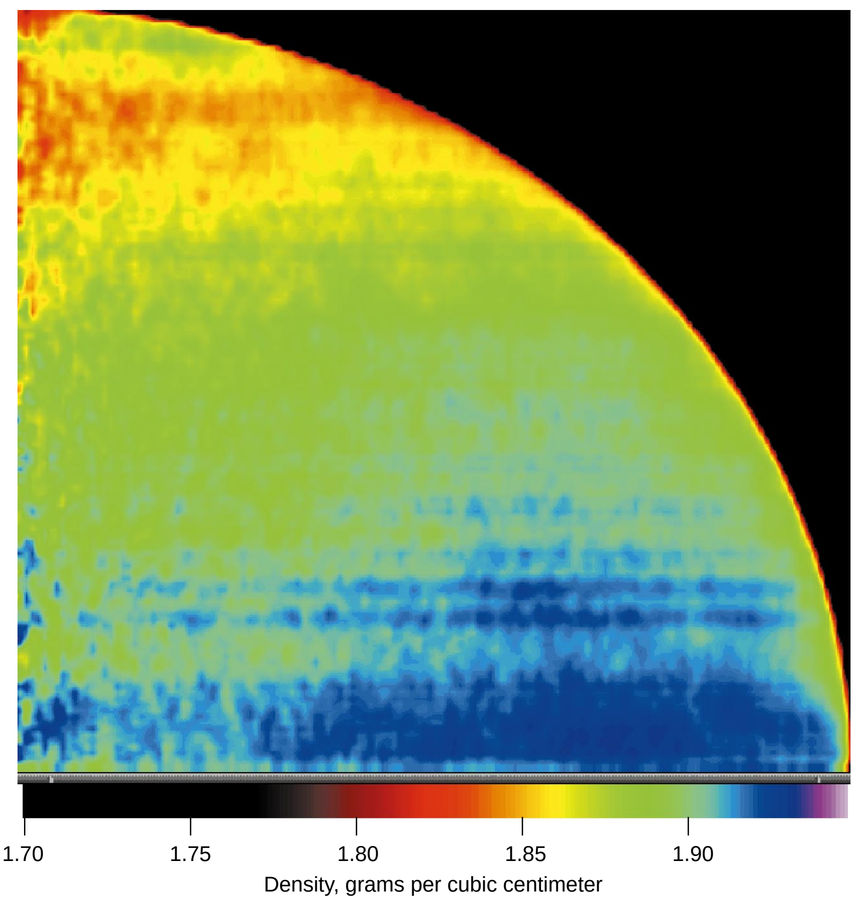


Figure 2. Using x-ray tomography, Livermore scientists led by Clint Logan have calculated the density distribution within a booster pellet made of ultrafine insensitive high-explosive powder (TATB). The pellet has a radius of 1.9 centimeters and weighs 26.1 grams.

An Explosive Issue

Many years ago, Livermore opted to use insensitive high explosives in its nuclear weapons for greater safety. An insensitive high-explosive component dropped during assembly or disassembly should not harm personnel, and a weapon that accidentally falls from a truck or even from an airplane should not detonate. But scientists are concerned that these high explosives might lose some of their safety advantage as they age. For example, voids in high explosives are necessary to drive the detonation wave. But if voids increase in size as the explosive ages, the explosive may become somewhat less safe. High explosives are therefore a primary focus of Livermore's work on aging weapons, and many experiments have been performed over the years.

Because the insensitive high explosive LX-17 is used in three of the four Livermore-designed weapons in the enduring stockpile, its reliability is paramount. Physicist Richard Howell and his colleagues under the leadership of George Overturf have conducted a number of experiments on LX-17 using positron-annihilation lifetime spectroscopy to search for interior voids and open volumes as small as several atomic bond lengths in diameter. (See *S&TR*, December 1998, pp. 13–17.) Overturf's team has used this method to measure changes in the microscopic, open-volume voids of LX-17's constituents, including the high-explosive powder TATB and its polymeric binder. His goal is to observe changes that occur as a result of temperature variations and environmental stresses during stockpile life.

Another experiment produced the first look at the density of a booster pellet (Figure 2). X-ray computed tomography was used to examine the density of a hemisphere of ultrafine high-explosive powder with no binder. This new tomographic technique is being used to correlate observed density variations with the material's age and its performance with measured density variations.

Extracting Gases

Over a period of years and at elevated temperatures, the many organic materials in a nuclear weapon eventually produce gases at detectable levels. There are two types of outgassing: the release of gases in the assembly room that become trapped in weapon cracks and crevices or dissolved in its organic components and the release of gases inside the weapon that are produced by chemical aging reactions, material interactions, or radiation. By either route, organic materials release compounds that can corrode metals and/or interact with and degrade other materials and components in the system. In general, outgassing signals the interaction and possible decomposition of materials in the warhead.

LeMay notes that just as surveillance scientists and engineers use nondestructive tools to assess changes in weapons without disassembling them, so do compatibility and aging scientists take advantage of nondestructive chemical tools to assess changes in weapon chemistry and compatibility.

One such tool is solid-phase microextraction (SPME, or "speemee"), which Livermore chemist David Chambers has adapted to examine gases for stockpile surveillance. A syringe needle containing a tiny, specially coated fiber is inserted into the headspace of a weapon to sample gases (Figure 3). Gas chromatography and mass spectrometry of the tiny sample then supply data on the contents of the weapon atmosphere. Unlike most other sampling techniques, SPME can deliver high-quality samples of the

Figure 3. A technician uses an early prototype of the solid-phase microextractor (the device between his hands) to take samples of gases produced by organic materials in a weapon's headspace. Analysis of the samples provides indications of material aging.

weapon's atmosphere to the gas chromatography port with little loss or dilution.

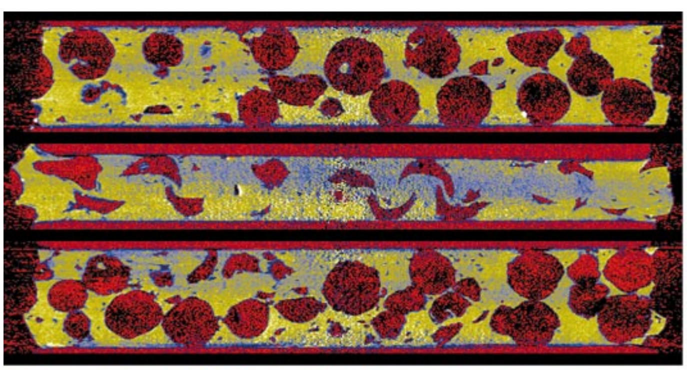
Livermore is the first laboratory to use SPME, a nondestructive technique, to examine weapon gases. With SPME, scientists can obtain an integrated chemical analysis of a weapon's interior environment, identifying potential material incompatibilities, identifying and monitoring aging indicators, and screening for defects such as incompletely cured adhesive and organic residues left over from assembly.

Chambers notes that with SPME, otherwise undetectable volatile gases are now detectable. For example, SPME was the first experimental method to reveal relatively large amounts of toluene in LX-17. Toluene is a solvent used in the synthesis of TATB, which is the primary ingredient in LX-17. After production, toluene remains trapped within TATB's crystalline structure. Experiments indicate that heating alone does not effectively liberate the toluene unless the LX-17 has been mechanically stressed. One experiment exposed TATB powder to ultrasonic energy and found a 500-fold increase in the level of toluene outgassing. Chambers believes that toluene levels can be monitored to determine the chemistry and stress-loading history of the high explosive.

Cushioning the Warhead

Cellular silicone stress cushions fill gaps between components, compensate for manufacturing tolerances of adjacent components, allow for thermal expansion of components and age-induced swelling of high explosives, and provide thermal insulation. For the cushions to perform these jobs successfully, they must exert a specific range of compressive forces at predetermined maximum and minimum gaps. Because the cushions fill gaps for the life of the weapon, the long-term stress behavior of the cushion under load in the chemical and radiation environment of a weapon is an ongoing concern.

LeMay has been examining aging in cellular silicone using a form of x-ray tomography developed at Livermore by materials scientist John Kinney. This technique reveals for the first time the internal structure of cushions under compression (Figure 4). It is now possible to see how some cells fold into one another to form "cups" and that cell wall "hinges" spring back after the load is removed. Some cells move to fill adjacent cells under compression. X-ray tomographic data can also be manipulated to show the shape of the cushions' pores. These images can be used, for example, to determine under what range of loads the pores remain interconnected, thus allowing gases and radiation to percolate through.



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Pressure = approximately 27.6×10^4 pascals (40 pounds per square inch), or about 35 percent compression

Unloaded

Figure 4. X-ray tomography is revealing for the first time the internal structure of cellular silicone cushions under compression. Note that some cells fold into one another, resulting in a structural change should the adjacent cell walls adhere to one another over time.

Because radiation from adjacent components is constantly bombarding the cushions and apparently percolating through them, LeMay and others are attempting to determine the damage it may be causing. Only preliminary data are available, because the researchers are still developing experimental tools that are sensitive enough to characterize radiation's effects.

Another Livermore chemist, Mehdi Balooch, used temperature-programmed desorption to study gases desorbed from silicone cushions. He found that at temperatures up to 500 kelvins, water desorbed at 100 micrograms per gram of silicone, with considerably less desorption of hydrogen, carbon monoxide, and carbon dioxide. The real concern was water, because silica, which makes up about 25 percent of the cushions, tends to adsorb water. Outgassing water vapor in a closed environment can migrate to other parts in the warhead and cause corrosion. This experiment—to further understand a fundamental property of a commonly used material in a weapon—demonstrates the need for basic science in the study of aging weapon materials.

Hydrogen: The Enemy Within

Balooch is also working with Wigbert Siekhaus to study the aging processes of uranium and lithium hydride. Specifically, they are studying the effects of such gases as water vapor and hydrogen on the surfaces of these materials: what the reactions are, what products are formed, and how the reactions depend on temperature, gas pressure, and the surface details. They have used atomic-force microscopy to get a close-up look at growths on the surface, modulated molecular-beam mass spectrometry to determine the gaseous reaction products and the rate of reactions, and temperature-programmed desorption to measure the quantity of adsorbed gases.

"Hydrogen is a major enemy of a weapon," according Balooch. It is generated in a weapon from several sources and attacks many components. Hydrogen is particularly damaging to uranium, reducing its capabilities. If a uranium surface is even slightly oxidized (a process that happens easily and quickly), it will adsorb hydrogen, prompting the growth of a form of corrosion known as hydride pitting along the uranium's grain boundaries (Figure 5). Scientists have had empirical evidence for the hydriding reaction for some time. But the reaction mechanism had never been studied in detail, and a general mechanism had not been identified.

A few years ago, Livermore researchers demonstrated the fundamental properties of the interaction of hydrogen and water vapor with clean uranium at room temperature and above. They measured the initial sticking probability (low for clean uranium), hydride formation probabilities, and desorption kinetics for hydrogen and water vapor.

A more recent experiment examined the interaction of hydrogen with uranium in the presence of impurities designed to mimic conditions in real systems. Tiny platinum particles measuring just 1 nanometer were deposited on a uranium surface. Platinum was used because it breaks hydrogen bonds to produce atomic hydrogen, hydrogen's most reactive form. When the uranium was exposed to hydrogen, hydrides formed in the vicinity of platinum clusters, expanding nonlinearly over time. Other impurities commonly found in uranium may also strongly influence hydriding reactions.

A major source of hydrogen in some nuclear devices is lithium hydride. The reaction of even trace amounts of water with lithium hydride generates hydrogen. The team has been using modulated molecular-beam mass spectrometry to study the kinetics of the water–lithium hydride reaction. As shown in Figure 6, the incoming beam of water vapor molecules and the outgoing hydrogen

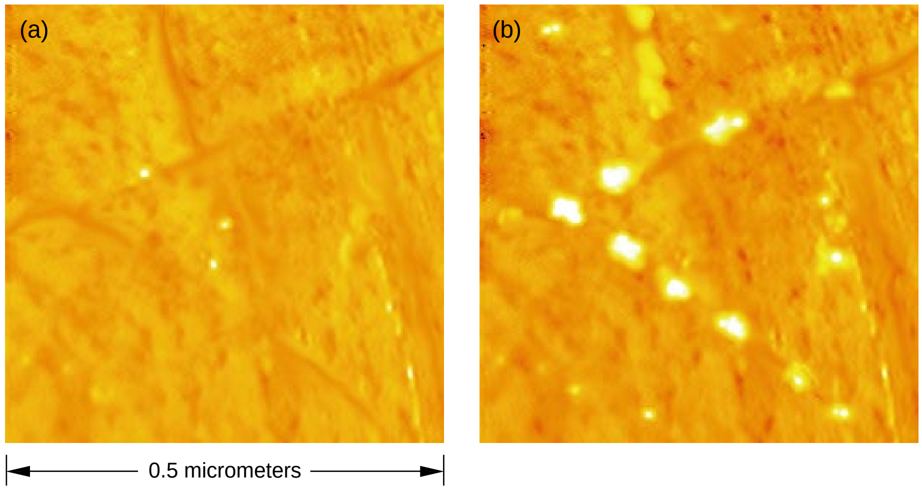

Figure 5. Atomic-force microscopy shows (a) uranium before hydriding takes place and (b) the formation of uranium hydride along grain boundaries, or hydride pitting.

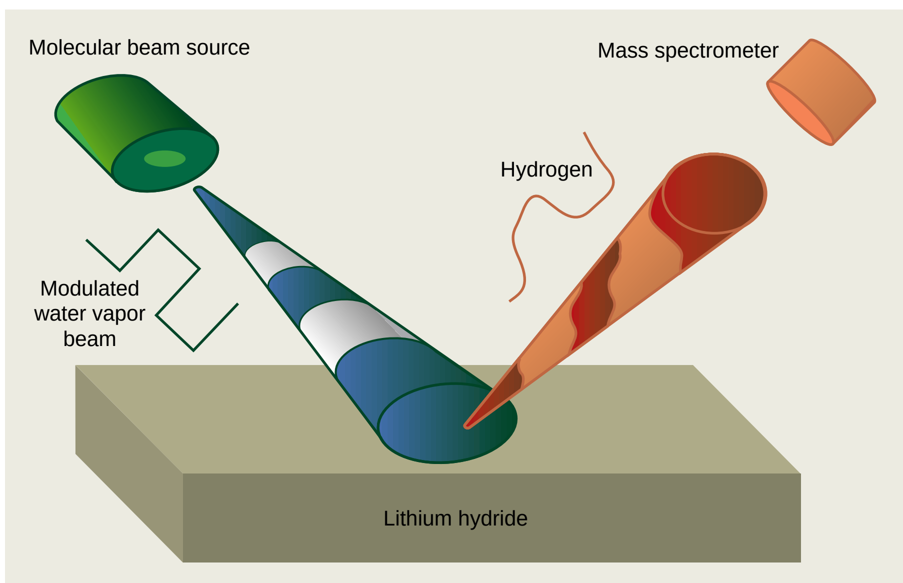

Figure 6. This schematic shows a modulated molecular-beam mass spectrometer being used to study the effects of water vapor on lithium hydride. The beam of water vapor directed at the lithium hydride is turned on and off at brief, regular intervals, as shown in the square pattern of the incoming beam. The outgoing beam of molecular hydrogen has a different shape, indicating a brief residence time in the lithium hydride.

molecular beam have different shapes, indicating a brief resident time in the lithium hydride. With these experiments, the team will be able to obtain basic information about lithium hydride and the reactions under way, including the sticking probability, reaction probability, elementary surface reaction steps, and diffusion rates.

Livermore is the only institution in the world using modulated molecular-beam techniques. Balooch, Siekhaus, and Alex Hamza developed the method about 20 years ago while they were at other institutions. According to Balooch, modulated molecular-beam experiments give the best chemical kinetic information.

Putting It All Together

Siekhaus notes that DOE weapons laboratories have detailed models for the multitude of reactions that take place immediately after a weapon is detonated but nothing comparable to describe the life of a weapon before detonation. With the relatively short shelf life that weapons used to have, such models were not necessary. But today they are.

Several years ago, chemist Dan Calef began developing a predictive model for one part of a nuclear device using data that the experimentalists have accumulated on lithium, uranium, gases, and other materials. As LeMay noted, excellent data are important to create such models. In a system as small and tight as a nuclear device, trace amounts and slow reactions matter. What seems to be a small issue can become magnified quickly.

According to Calef, "Until recently, decisions about lifetimes tended to be based on expert opinion and experience. Our goal is to make these decisions from a science-based standpoint."

His first task is to model the transport of gases around the system. The originally designed geometry of the weapon system and all available experimental data are going into ALE3D, a Livermore hydrodynamic code. He will then examine all the chemical reactions that occur over time and how these processes change the designed geometry. Figure 7 shows a structural change that results from mass diffusion.

Calef is particularly interested in the small details in the system, such as pores and gaps between components. It is in those minute spaces that such critical activities as diffusion and destructive surface chemistry take place. With this close-up view, he can

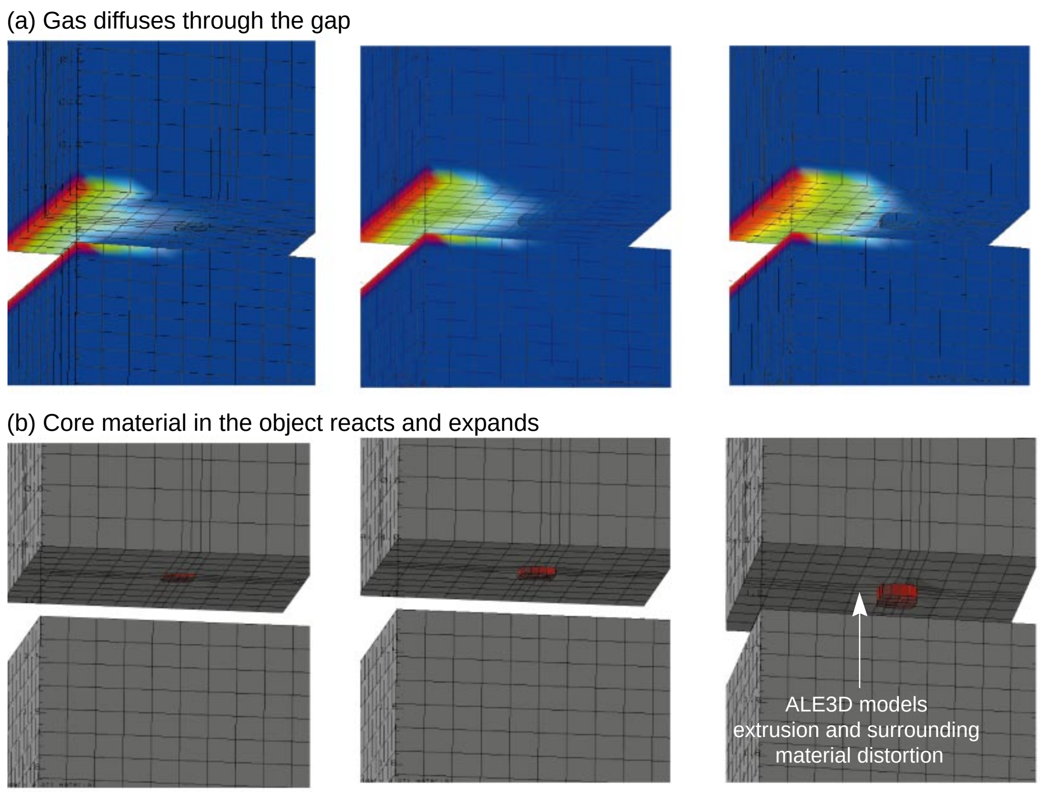

Figure 7. Mass diffusion and structural distortion as shown in an ALE3D model. In this calculation, (a) a solid object reacts with a gas diffusing through a gap. (b) The reacted solid has a lower density and expands.

determine where problem areas might be. From there, he will define any life-limiting components and determine the lifetime of the system.

Livermore weapon models already contain considerable detail, but the detail is of idealized materials. When the models are based on data from actual constituent materials and real chemical reactions, they will be much more useful. They can be tweaked to show what effect temperature changes, shock, vibration, and other influences have on a weapon. Identifying weak points for further experimentation can help to prioritize future research and development activities. Models could also help to identify which parts need to be replaced and when.

LeMay notes that his group and others at Livermore must continually refine their approach to characterizing and modeling the aging of Livermore's weapon materials. As with any modeling program, there is a strong dynamic between predictive efforts and continued experimentation. Even with the most powerful computers, modeling needs validation from experimental results in an ongoing, iterative process that constantly refines modeling results and methods.

LeMay and his colleagues will constantly be integrating their improved understanding of the aging process into weapon codes so that changes at the system level can be effectively assessed. LeMay concludes that the goal of science-based stockpile stewardship—maintaining high confidence in the safety and reliability of Livermore's weapons without nuclear testing—requires constant vigilance.

—Katie Walter

Key Words: ALE3D, core surveillance, enhanced surveillance, materials science, modeling, modulated molecular-beam spectroscopy, positron-annihilation lifetime spectroscopy, solid-phase microextraction (SPME), surface chemistry, x-ray tomography.

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About the Scientist

JAMES LEMAY received his B.S. in chemistry in 1980 and his Ph.D. in polymer science in 1984, both from the University of Akron. He began working at Livermore in 1984. In 1991, he became Livermore's lead scientist for material compatibility issues. He has supported the W89 and W87 weapon programs, dismantlement of the W48 and W79 weapons, stockpile storage issues, and core surveillance activities. He is currently a program element leader for weapon materials compatibility and aging in the Chemistry and Materials Science Directorate and is a research and development focus area leader in the Enhanced Surveillance Program. In 1998, he received a Department of Energy Nuclear Weapons Program award for technical excellence in weapon materials.